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Foreign Technology Division
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by

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The equation of state describing the experimental data within the temperature range of 273.15 to 773.15°K and a pressure up to 400 bars was obtained as a result of processing experimental data with respect to the compressibility of helium, nitrogen, and mixtures of them on a digital computer. Comparison of the calculated values of the coefficients of compressibility and density of the mixture of helium with nitrogen calculated by the proposed equation of state with the experimental values demonstrates satisfactory comparison in the entire temperature and pressure range encompassed by the experiment.
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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

EQUATION OF THE STATE OF A HELIUM AND NITROGEN MIXTURE

V. N. Popov, V. I. Chernyshov

(Moscow)

As a result of the digital computer processing of the experimental data on the compressibility of helium, nitrogen and their mixtures, an equation of state which describes the experimental data in the 273.15-773.15°K temperature interval and under a pressure of 400 bar, was obtained.

A comparison of the calculated values of the coefficients of compressibility and density of a mixture of helium and nitrogen, calculated by the proposed equation of state, with the experimental data shows a satisfactory coincidence in the entire temperature and pressure region, encompassed by the experiment. Tables 5, Bibliographical entries 18, Pages 162-165.

A mixture of helium and nitrogen is employed in technology as a heat-transfer agent, thus for carrying out hydrodynamic calculations and solving many heat-exchange problems it is necessary to have reliable data available on the thermal, calorific properties, and also on the transfer properties of this mixture in a broad range of variation of the parameters of state.

In the present article by the digital computer processing of the experimental data [1-4] for helium, nitrogen, their mixtures, equations of state were obtained, by which detailed tables of the values of the coefficients of compressibility and density were computed in the temperature range from 273.15 up to 773.15°K and in the pressure range from 50 to 400 bar.

Equation of the State of Helium. For the processing of all the experimental data on helium in the temperature and pressure intervals examined by us, an equation of state in the form of a polynomial for degrees of density was employed

$$z = 1 + B_{11}\rho + C_{111}\rho^2. \qquad (1)$$

The dependences $B_{11} = f(T)$ and $C_{111} = f(T)$ were approximated by a polynomial for the degrees $\tau = 1000/T$

$$B_{11}(T) = B_{11}^0(T) + \sum_{i=0}^{5} b_i\tau^i, \qquad (2)$$

$$C_{111}(T) = \sum_{i=0}^{2} c_i\tau^i. \qquad (3)$$

The coefficients of these dependences were determined on a digital computer by the method of least squares in two variables for the whole aggregate of available experimental data for helium [5-11], also including our experimental data [3]. The values of coefficients b_i and c_i are given in Table 1. Dependence $B_{11}^0(T)$ is taken in accordance with [12] and has the form:

$$B_{11}^0(T) = \left(0{,}001801 + \frac{0{,}02169\tau}{1 + 1{,}89\tau}\right). \qquad (4)$$

A total of 254 experimental points were taken for processing. The deviations of the calculated values of the coefficient of compressibility from the experimental values for 188 points were less than ±0.05%, for 47 points less than ±0.10% and for 19 points less than ±0.25%.

Table 1. The values of the coefficients of polynomials (2) and (3) for helium.

$b_i \cdot 10^4$, m^3/kmole	b_0	+0,45730
	b_1	+1,41850
	b_2	−0,36636
$c_i \cdot 10^6$, $m^6/(kmole)^2$	c_0	+0,34964
	c_1	+6,58490
	c_2	−0,90130

The equation of state of nitrogen. In composing the equation of state for nitrogen we used experimental data [13-15], which encompasses the temperature and pressure intervals examined by us and also our experimental data [2, 4]. The equation of state was composed in two stages. In the first stage, the graphico-analytical method was used, which was examined as a first approximation. For approximating the dependence of the second virial coefficient $B_{22}{}^0(T)$ on temperature for the whole aggregate of experimental data [7, 13, 15, 16] with respect to $B_{22}{}^0(T)$ a polynomial for degrees of τ was selected

$$B_{22}{}^0(T)=\sum_{i=0}^{4} b_i/\tau^i. \tag{5}$$

The values of the coefficients of b_i are given in Table 2. In the second stage the final equation of state is used in the form

$$z = 1 + B_{22}\rho + C_{222}\rho^2 + D_2\rho^3 + E_2\rho^4. \tag{6}$$

Dependences $B_{22}(T)$, $C_{222}(T)$, $D_2(T)$ and $E_2(T)$ were approximated by a polynomial for degrees $\tau = 1000/T$

$$B_{22}(T) = B_{22}{}^0(T),$$

$$C_{222}(T)=\sum_{i=0}^{4} c_i\tau^i, \qquad D_2(T)=\sum_{i=0}^{4} d_i\tau^i, \qquad E_2(T)=\sum_{i=0}^{4} e_i\tau^i. \tag{7}$$

The coefficients of these dependences (7) were determined on a digital computer by the method of least squares for the whole aggregate of available experimental points for nitrogen. The values of the coefficients of c_i, d_i, ε_i are given in Table 3.

Table 2. The values of the coefficients b_i of polynomial (5) for nitrogen.

$b_i \cdot 10^5$ m^3/kmole	b_0	−0,14873
	b_1	+0,91396
	b_2	−2,23460
	b_3	+2,05920
	b_4	−0,82300

Table 3. The values of the coefficient of the polynomials (7) in the equation of state for nitrogen.

$c_i \cdot 10^2$, $m^6/(\text{kmole})^2$	c_0	−0,62141
	c_1	+0,86687
	c_2	−0,42191
	c_3	+0,10118
	c_4	−0,00958
$d_i \cdot 10^2$ $m^9/(\text{kmole})^3$	d_0	+0,14604
	d_1	−0,11465
	d_2	+0,028960
	d_3	−0,002310
	d_4	0,00000
$\varepsilon_i \cdot 10^3$ $m^{12}/(\text{kmole})^4$	ε_0	−0,14232
	ε_1	+0,12606
	ε_2	−0,035740
	ε_3	+0,00325
	ε_4	+0,00002

A total of 140 experimental points were taken for processing. The deviations of the calculated values of the coefficient of compressibility from the experimental values for 114 points was less than ±0.05%, for 17 points less than ±0.10% and for 9 points less than ±0.25%.

The equation of state of a mixture of helium and nitrogen. For composing the equation of state of a mixture in virial form the processing of the experimental data was carried out in two stages. In the first stage the graphico-analytical method of processing was used, which was examined as a first approximation. This method is described in detail in work [2].

For the final processing of the experimental data [2, 4, 15] in the temperature range 273.15-773.15°K and pressure range 50-400 bar an equation in the form of a polynomial for degrees of density was selected

$$z_{\text{cm}} = 1 + B_{\text{cm}}\rho + C_{\text{cm}}\rho^2 + D_{\text{cm}}\rho^3 + E_{\text{cm}}\rho^4. \qquad (8)$$

Functions B_{CM}, C_{CM}, D_{CM}, E_{CM}, have the following form:

$$\begin{aligned} B_{\text{cm}}(T, x) &= B_{11}x_1^2 + 2B_{12}x_1x_2 + B_{22}x_2^2, \\ C_{\text{cm}}(T, x) &= C_{111}x_1^3 + 3C_{112}x_1^2x_2 + 3C_{122}x_1x_2^2 + C_{222}x_2^3, \\ D_{\text{cm}}(T, x) &= \gamma_1(1-x_1) + (D_2-\gamma_1)(1-x_1)^2 + \gamma_2(1-x_1)^2x_1, \\ E_{\text{cm}}(T, x) &= \alpha_1(1-x_1) + (E_2-\alpha_1)(1-x_1)^2. \end{aligned} \qquad (9)$$

The dependence of the second virial coefficient B_{12} on temperature for a mixture is approximated by the polynomial

$$B_{12}(T) = \sum_{i=0}^{3} b_i \tau^i, \text{ cm}^3/\text{mole}. \tag{10}$$

The coefficients of b_i were determined on a digital computer by the method of least squares for the whole aggregate of available experimental data [15-18] with respect to $B_{12}(T)$, which are given in Table 4. For approximating $C_{112}(T)$, $C_{122}(T)$, $\gamma_1(T)$, $\gamma_2(T)$, $\alpha_1(T)$ a polynomial for degrees of $1/\tau$ was selected

$$C_{112}(T) = \sum_{i=0}^{3} (c_i/\tau^i), \text{ m}^6/(\text{kmole})^2,$$

$$C_{122}(T) = \sum_{i=0}^{3} (c_i'/\tau^i), \text{ m}^6/(\text{kmole})^2,$$

$$\gamma_1(T) = \sum_{i=0}^{3} (d_i/\tau^i), \text{ m}^9/(\text{kmole})^3, \tag{11}$$

$$\gamma_2(T) = \sum_{i=0}^{3} (d_i'/\tau^i), \text{ m}^9/(\text{kmole})^3,$$

$$\alpha_1(T) = \sum_{i=0}^{3} (e^i/\tau^i), \text{ m}^{12}/(\text{kmole})^4.$$

The coefficients of these dependences were determined on a digital computer by the method of least squares in three variables for the whole aggregate of available experimental data with respect to compressibility for a mixture of helium and nitrogen [2, 4, 15], also including our experimental data. The values of the coefficients are given in Table 5.

Table 4. Values of the second virial coefficient $B_{12}(T)$ for mixtures of helium and nitrogen according to the data of various authors.

T, °K	273,15	298,15	303,15	373,15	448,15		523,15	598,15		673,15	748,15	
cm^3/mole	21,63	22,08	21,83	22,49	22,82	22,92	21,41	21,72	22,20	21,20	20,33	21,27
Author	[17]	МЭИ	[16]	МЭИ	МЭИ	[15]	[15]	[15]	МЭИ	[15]	[15]	МЭИ

Table 5. Values of the coefficients of polynomials (11) in the equation of state for a helium-nitrogen mixture.

b_i, cm^3/mole	b_0	+6,87490
	b_1	+17,0850
	b_2	−5,87540
	b_3	+0,63099
$c_i \cdot 10^2$, $m^6/(kmole)^2$	c_0	+0,25786
	c_1	−0,85548
	c_2	+0,34218
	c_0'	−0,17026
	c_1'	+0,94896
	c_2'	−1,06670
$d_i \cdot 10^2$, $m^9/(kmole)^3$	d_0	+0,03981
	d_1	−0,42416
	d_2	+1,02320
	d_0'	+0,07720
	d_1'	−0,16915
	d_2'	−0,16507
$e_i \cdot 10^3$, $m^{12}/(kmole)^4$	e_0	−0,11255
	e_1	+0,72084
	e_2	−1,19520

The temperature functions for the pure components were calculated with equations (2), (3), (7). At a zero concentration of one of the components of the mixture the equation of state of the mixture (8) turns into the equation of state of the other pure component.

A total of 133 experimental points were taken for processing. The deviation of the calculated values of the coefficient of

compressibility from the experimental values for 76 points was less than ±0.05%, for 37 points less than ±0.10%, for 18 points less than ±0.20% and for only 2 points the deviation was more than 0.20%.

A comparison of the calculated values of the coefficients of compressibility and density of a mixture of helium and nitrogen, computed by equation of state (8), with the experimental values [2, 4, 15] shows a satisfactory correspondence in the entire temperature and pressure region, encompassed by the experiment. This makes it possible to expect, that in the whole temperature region 273.15-773.15°K at pressures of up to 400 bar the proposed equation of state will make it possible to obtain reliable and accurate data for the caloric properties of a mixture of helium and nitrogen.

Conclusions. 1. The equations of state for helium, nitrogen and their mixtures describe the available experimental data for helium and nitrogen within limits of ±0.01%, and for mixtures of helium and nitrogen ±0.2%.

2. The values of the coefficients of compressibility and density in temperature interval 273.15-773.15°K and pressure interval 50-400 bar, computed with the equation of state for a mixture of helium and nitrogen, can be used for calculating technological processes and solving planning and design problems.

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